PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Thermocouples

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to thermocouples.

It is known that a measure of the efficiency of a thermocouple when used in a device such as a thermoelectric refrigerator or generator is given by a figure of merit θ, defined as

$$\frac{|\eta_1-\eta_2|\sqrt{T}}{\sqrt{\lambda_1\rho_1}+\sqrt{\lambda_2\rho_2}},$$

where the suffixes 1 and 2 refer respectively to the two elements of the thermocouple, T is the arithmetic mean of the absolute temperatures of the hot and cold junctions of the thermocouple, and η, λ, and ρ are respectively the thermoelectric power, thermal conductivity and electrical resistivity of an element measured at the temperature T in the direction of the length of the element between the hot and cold junctions. The present invention is based upon an investigation of the conditions under which optimum values of the figure of merit θ are obtained for thermocouples in which the elements are composed of the semiconductor bismuth telluride (Bi_2Te_3), the elements being respectively of P-type and N-type conductivity; it will be appreciated that for such a thermocouple the thermoelectric powers η_1 and η_2 are of opposite sign.

One factor which must be taken into account in such an investigation is the anisotropy displayed by bismuth telluride in respect of certain of its physical properties. The compound crystallises in the trigonal system, and a crystal of bismuth telluride can be cleaved easily in planes perpendicular to the principal crystal axis. It has been found for both P-type and N-type bismuth telluride that, of the properties concerned in the expression for θ, the thermoelectric power η is substantially isotropic, while both the thermal conductivity λ and the resistivity ρ vary appreciably in accordance with the inclination to the principal crystal axis of the direction in which they are measured. The inventor has found that the product of the thermal conductivity and the resistivity is at a minimum for directions perpendicular to the principal crystal axis, that is to say parallel to the cleavage planes; thus in order to obtain the highest values for the figure of merit θ for a thermocouple comprising elements composed respectively of P-type and N-type bismuth telluride, it is necessary that both elements should consist of one or more crystals for each of which the principal crystal axis is disposed substantially perpendicular to the direction of the length of the element between the hot and cold junctions.

A further factor which it is necessary to consider is the impurity content of the elements of the thermocouple, since the properties of semiconductors such as bismuth telluride are profoundly affected by the inclusion of donor and/or acceptor impurities. In this connection it is convenient, as is common in the semiconductor art, to refer to the impurity content in terms of the resistivity of the material; as is well known, the resistivity of a semiconductor at a given temperature decreases with increase of the net significant impurity concentration (that is to say the difference between the donor impurity concentration and the acceptor impurity concentration). For a thermocouple with P-type and N-type bismuth telluride elements in which the crystals are orientated as described above, the inventor has found that, for a mean operating temperature T of 293° K., the maximum value for the figure of merit θ is obtained when resistivity of the P-type element is 1.15 milliohm centimetres and the resistivity of the N-type element is 1.05 milliohm centi-

metres (each of these resistivities of course being measured in the direction of the length of the relevant element, as are other resistivities referred to below); the maximum value of θ for this temperature is 0.76, when the thermoelectric power η is expressed in volts/°C., the thermal conductivity λ is expressed in watts/cm.°C., and the resistivity ρ is expressed in ohm centimetres. Near the maximum, the value of θ does not vary very rapidly as the resistivities of the P-type and N-type elements are varied; if a lower limit for the value of θ of 90% of its maximum value is set, it is found that the condition for θ to have a greater value than this lower limit can be expressed with good accuracy, for a mean operating temperature of 293°K., as

$$(\rho_P - 1.23)^2 + (\rho_N - 1.28)^2 \leqslant 1.14,$$

where ρ_P and ρ_N are the respective resistivities (measured at 293°K.) of the P-type and N-type elements expressed in milliohm centimetres.

Finally, it is necessary to consider the variation of the figure of merit θ as the mean operating temperature T is varied, since the properties of bismuth telluride vary with temperature. For mean operating temperatures below 293°K., the maximum value of θ is lower than the maximum value for a mean operating temperature of 293°K., but the optimum range of resistivities for the two elements can be defined by the same expression as given above for a mean operating temperature of 293°K., but with the resistivities ρ_P and ρ_N being as measured at the mean operating temperature. For mean operating temperatures above 293°K., the maximum value of θ increases initially as the mean operating temperature is increased, but in this case the optimum range of resistivities for the elements also varies; it is found that for mean operating temperatures between 293°K. and 373°K., the optimum range can be defined by the condition

$$(\rho_P - 2.87 + 0.0056\,T)^2 + (\rho_N - 2.92 + 0.0056\,T)^2 \leqslant (2.54 - 0.005\,T)^2$$

where ρ_P and ρ_N are the respective resistivities (measured at the mean operating temperature T°K.) of the P-type and N-type elements, expressed in milliohm centimetres.

It must be noted that the expressions given above can be considered valid only if the temperature difference between the hot and cold junctions of the thermocouple does not exceed about one quarter of the absolute value of the mean operating temperature.

Thus, in accordance with the foregoing analysis, the present invention consists in a thermocouple comprising elements respectively composed of P-type and N-type bismuth telluride, each element consisting of one or more crystals for each of which the principal crystal axis is disposed substantially perpendicular to the direction of the length of the element between the hot and cold junctions, and the P-type and N-type elements having, at some temperature (T°K.) not greater than 373°K., respective resistivities ρ_P and ρ_N milliohm centimetres, measured in the respective directions of the lengths of the elements, such that the expression

$$[1.14 - (\rho_P - 1.23)^2 - (\rho_N - 1.28)^2]$$

has a value not less than zero if T is not greater than 293, or such that the expression

$$[(2.54 - 0.005T)^2 - (\rho_P - 2.87 + 0.0056T)^2 - (\rho_N - 2.92 + 0.0056T)^2]$$

has a value not less than zero if T is greater than 293, whereby the thermocouple is suitable for operation with the hot and cold junctions respectively at temperatures $(T+\Delta T)$°K and $(T-\Delta T)$°K, where ΔT is not greater than $\frac{1}{8}$T.

Elements for thermocouples in accordance with the invention may be prepared in the following manner. Bismuth and tellurium in proportions corresponding to stoichiometric bismuth telluride are placed in a cylindrical silica bomb, together with a small quantity of either iodine or lead, which respectively act as donor and acceptor impurities in bismuth telluride, and are respectively added according to whether N-type or P-type material is to be produced. The bomb is evacuated to produce inside it a vacuum corresponding to a pressure of less than 10^{-5} millimetres of mercury, and is then sealed; when iodine is used, the evacuation period is standardised at 15 minutes, in order to make consistent allowance for the volatilisation of iodine which occurs.

The sealed bomb is then heated at a temperature of 900°C. for at least three hours, in order to bring about complete formation of the bismuth telluride and uniform distribution of the impurity. After cooling to room temperature and removal from the bomb, the charge is loaded into an elongated silica boat, is then just melted by high frequency induction heating under an inert atmosphere so that it takes up the shape of the boat, and is immediately cooled to room temperature to form a solid ingot.

The solid ingot in the boat is then subjected to the process known as "single pass zone melting," in which a molten zone is formed at one end of the ingot and is caused to traverse the whole length of the ingot; the

process is carried out under a slow flow of inert gas at atmospheric pressure, and the rate of advance of the molten zone along the ingot may conveniently be of the order of one inch per hour.

An ingot produced in this manner is found to consist of one or more crystals for each of which the principal crystal axis is disposed perpendicular to the longitudinal axis of the ingot; it should be noted that in the case of a polycrystalline ingot the principal crystal axes of the various crystals are not necessarily parallel to each other. The elements of one conductivity type for a series of thermocouples are then cut from such an ingot so that the directions of their lengths are parallel to the longitudinal axis of the ingot.

For producing N-type material with a resistivity in the appropriate range at a temperature of 293°K, the proportion of iodine in the original constituents should lie in the range of about 0.07—0.16% by weight, and for producing P-type material with a resistivity in the appropriate range at a temperature of 293°K, the proportion of lead in the original constituents should lie in the range of about 0.03—0.12% by weight. For producing material suitable for use at other temperatures, somewhat different proportions of either iodine or lead in the original constituents may be required, but the necessary amount may be readily determined empirically in each case.

WHAT WE CLAIM IS:—

1. A thermocouple comprising elements respectively composed of P-type and N-type bismuth telluride, each element consisting of one or more crystals for each of which the principal crystal axis is disposed substantially perpendicular to the direction of the length of the element between the hot and cold junctions, and the P-type and N-type elements having, at some temperature (T°K) not greater than 373°K, respective resistivities ρ_P and ρ_N milliohm centimetres, measured in the respective directions of the lengths of the elements, such that the expression

$$[1.14-(\rho_P-1.23)^2-(\rho_N-1.28)^2]$$

has a value not less than zero if T is not greater than 293, or such that the expression

$$[(2.54-0.005T)^2-(\rho_P-2.87+0.0056T)^2-(\rho_N-2.92+0.0056T)^2]$$

has a value not less than zero if T is greater than 293.

2. A thermocouple according to Claim 1, in which each element has been cut from an elongated ingot of bismuth telluride of appropriate conductivity type, which has been subjected to the process known as "zone melting," in such a manner that the direction of the length of the element is parallel to the longitudinal axis of the ingot.

For the Applicants,
W. J. C. CHAPPLE,
Chartered Patent Agent.

PROVISIONAL SPECIFICATION

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appreciably in accordance with the inclination to the principal crystal axis of the direction in which they are measured. The inventor has found that the product of the thermal conductivity and the resistivity is at a maximum for directions perpendicular to the principal crystal axis, that is to say parallel to the cleavage planes; thus in order to obtain the highest values for the figure of merit θ for a thermocouple comprising elements composed respectively of P-type and N-type bismuth telluride, it is necessary that both elements should consist of one or more crystals for each of which the principal crystal axis is disposed substantially perpendicular to the direction of the length of the element between the hot and cold junctions.

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$$(\rho_P - 1.23)^2 + (\rho_N - 1.28)^2 \leqslant 1.14,$$

where ρ_P and ρ_N are the respective resistivities (measured at 293°K) of the P-type and N-type elements expressed in milliohm centimetres.

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$$(\rho_P - 2.87 + 0.0056\,T)^2 + (\rho_N - 2.92 + 0.0056\,T)^2 \leqslant (2.54 - 0.005\,T)^2$$

where ρ_P and ρ_N are the respective resistivities (measured at the mean operating temperature T °K of the P-type and N-type elements, expressed in milliohm centimetres.

It must be noted that the expressions given above can be considered valid only if the temperature difference between the hot and cold junctions of the thermocouple does not exceed about one quarter of the absolute value of the mean operating temperature.

Thus, in accordance with the foregoing analysis, the present invention consists in a thermocouple comprising elements respectively composed of P-type and N-type bismuth telluride, the thermocouple being intended for operation with the hot and cold junctions respectively at temperatures $(T+\Delta T)$°K and $(T-\Delta T)$°K, where T is not greater than 373 and ΔT is not greater than $\frac{1}{8}$T, each element consisting of one or more crystals for each of which the principal crystal axis is disposed substantially perpendicular to the direction of the length of the element between the hot and cold junctions, and the P-type and N-type elements respectively having resistivities ρ_P and ρ_N milliohm centimetres such that

$$(\rho_P - 1.23)^2 + (\rho_N - 1.28)^2 \leqslant 1.14$$

where T is $\leqslant$293, and

$$(\rho_P - 2.87 + 0.0056\,T)^2 + (\rho_N - 2.92 + 0.0056\,T)^2 \leqslant (2.54 - 0.005\,T)^2$$

where $293 \leqslant T \leqslant 373$.

Elements for thermocouples in accordance with the invention may be prepared in the following manner. Bismuth and tellurium in proportions corresponding to stoichiometric bismuth telluride are melted, together with a small proportion of a donor or acceptor impurity to determine the conductivity type and resistivity of the material, in an evacuated tubular silica container, the melt then being allowed to cool to solidify the bismuth telluride in the form of an ingot. The ingot is then removed from the container and is subjected to the process known as zone melting, in which a molten zone is formed at one end of the ingot and is caused to traverse the whole length of the ingot, the process being carried out under a slow flow of inert gas at atmospheric pressure. The rate of advance of the molten zone along the ingot may conveniently lie between half an inch and one inch per hour. An ingot produced in this manner is found to consist of one or more crystals for each of which the principal crystal axis is disposed perpendicular to the longitudinal axis of the ingot; it should be noted that in the case of a polycrystalline ingot the principal crystal axes of the various crystals are not necessarily parallel to each other. The elements of one conductivity type for a series of thermocouples are then cut from such an ingot so that the directions of their lengths are parallel to the longitudinal axis of the ingot.

A suitable donor impurity for use in bismuth telluride is iodine, and a suitable acceptor impurity is lead. For producing N-type material with a resistivity in the appropriate range at a temperature of 293°K, the concentration of the iodine in the original melt should be of the order of 0.07—0.16% by weight, and for producing P-type material with a resistivity in the appropriate range at a temperature of 293°K, the concentration of the lead in the original melt should be of the order of 0.03—0.12% by weight.

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